HYDROBORATION OF ALKENES AND ALKYNES WITH SODIUM BOROHYDRIDE CATALYZED BY TITANIUM COMPLEX

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The titanium complex prepared from Cp<sub>2</sub>TiCl<sub>2</sub> and NaBH<sub>4</sub> in THF in the presence of crown ethers efficiently promotes the catalytic hydroboration of alkenes and alkynes with NaBH<sub>4</sub> to give sodium alkyl- and alkenyl-borohydrides which are converted into alcohols and alkenes, respectively.

Crown ethers have found wide application as catalysts in a variety of organic reactions.<sup>1)</sup> However, the utility of crown ethers in organotransition metal chemistry has little been explored. Previously, we have reported that the titanium complex generated by the reaction of  $Cp_2TiCl_2$  with LiBH<sub>4</sub> catalytically promotes the hydroboration of alkenes with LiBH<sub>4</sub> in THF to give lithium alkyl-borohydrides.<sup>2)</sup> However, under the same reaction conditions, NaBH<sub>4</sub>, which is less expensive but less soluble in THF than LiBH<sub>4</sub>, is not an efficient reagent for this reaction. We now report that when the reaction is carried out in the presence of a crown ether, the catalytic hydroboration of alkenes and alkynes occurs smoothly by using NaBH<sub>4</sub>. Alkylborohydrides thus produced are converted to alcohols on oxidation and alkenylborohydrides to alkenes on protonolysis. Thus, this work constitutes an example of the utility of crown ethers in transition metal catalyzed reactions.

A typical procedure of the hydroboration-oxidation reaction of alkenes is illustrated in the conversion of styrene to phenylethanols: A freshly recrystallized  $Cp_2TiCl_2$  (0.51 mmol) was added to a mixture of  $NaBH_4$  (2.65 mmol) and 18-crown-6 (0.49 mmol) in THF (10 ml) and the mixture was stirred for 1 h at 65 °C



under argon atmosphere. During this period, the color of the mixture changed from gray to violet with evolution of H<sub>2</sub>. Styrene (2,60 mmol) was added, and the mixture was stirred for 5 h at the same temperature. A 3 mol dm<sup>-3</sup> methanolic CH<sub>3</sub>ONa solution (3 ml), subsequently 30% aqueous H<sub>2</sub>O<sub>2</sub> (5 ml) were added to the mixture. After being stirred for 0.5 h, the resulting mixture was extracted with diethyl ether. The extract was dried and concentrated. The GLC analysis of the residue using dodecane as an internal standard showed that the reaction mixture contains 1- and 2-phenylethanols (70%) in a 69:31 ratio along with a trace amount of unreacted styrene.

The efficiency of this reaction varied with metal cations in metal borohydrides and crown ethers employed. The results are given in Table 1. The combination of NaBH4 and 18-crown-6<sup>3</sup>) was found to be an efficient reagent system for the hydroboration in THF. The conversion of styrene to phenylethanols was conducted by using the reagent system consisting of various amounts of NaBH4, 18-crown-6, and styrene. The results are given in Table 2. The hydroboration of styrene occurred catalytically with respect to titanium and 18-crown-6. The ratio of 1-phenylethanol/2-phenylethanol was almost independent of composition of the reagents in the reaction system and of the reaction time.

In a similar manner, various alkenes were converted to the corresponding alcohols. The results are listed in Table 3.

Striking features of this hydroboration-oxidation reaction may be summarized as follows: (1) The crown ether, 18-crown-6, mediates the formation of a reactive titanium complex from Cp<sub>2</sub>TiCl<sub>2</sub> and NaBH<sub>4</sub> and also the subsequent catalytic hydroboration of alkenes with NaBH<sub>4</sub>; in the absence of 18-crown-6, both the complex formation and the catalytic hydroboration hardly occur. (2) Initial products of the reaction are not alkylboranes but sodium alkylborohydrides.<sup>2</sup>) (3) The hydroboration takes place preferentially in an anti-Markownikoff fashion.

Possible pathways of the catalytic reaction are outlined in Scheme 2. The titanium complex 1 is formed by the reaction of the Na-crown complex 3 with Cp<sub>2</sub>TiCl<sub>2</sub>,

Hydroboration-Oxidation Reaction of Styrene"						
Borohydride	Crown ether	Reaction time / h	Color	Yield of Phenyl- ethanols / % <sup>b)</sup>		
LiBH4	None	5	Violet	70		
LiBH4	12-crown-4	5	Violet	77		
NaBH4	None	24	Red	trace		
NaBH4	12-crown-4	24	Brown	<1		
NaBH4	15-crown-5	24	Violet	59		
NaBH <sub>4</sub>	18-crown-6	5	Violet	70		
KBH4	12-crown-4	24	Brown	<1		
KBH4	15-crown-5	24	Violet	20		
KBH4	18-crown-6	5	Violet	20		

Table 1.	Effects	of	Metal	Borohyd	drides	and	Crown	Ethers	on	the
	Hydrobor	at:	ion-Oxi	idation	React	ion d	of Styr	cene <sup>a)</sup>		

a) All the reactions were conducted at 65 °C in THF by using the reagent system; styrene : MBH4 : Cp2TiCl2 : crown ether = 5 : 5 : 1 : 1.

b) Yields were determined by GLC and based on styrene used.

hydroboration-oxidation Reaction of Styrene								
	Molar	ratio		Reaction	Total	Ratio	of	
Cp <sub>2</sub> TiCl	2:NaBH4:1	8-crown-	6:styrene	time / h	yield / % <sup>D)</sup>	2-ol /	1-ol	
0	5	1	5	5	0			
1	5	0	5	5	0			
1	3	1	3	3	77 (237)	26	74	
1	3	3	3	3	77 (231)	31	69	
1	5	1	5	5	70 (359)	31	69	
1	10	1	10	24	42 (429)	30	70	
1	20	1	20	24	38 (798)	26	74	
1	20	1	20	48	49(1030)	26	74	

Table 2. Effects of Reagent System and Reaction Conditions on the Hydroboration-Oxidation Reaction of Styrene<sup>a</sup>)

a) All the reactions were conducted at 65 °C in THF. b) GLC yields based on styrene used. Figures in parentheses indicate the yields based on Cp2TiCl2 used.

Yield / %<sup>b)</sup> Ratio of Reaction Product(s) Alkene 1-01/2-01 time / h 94 1-Octene 24 1-Octanol 72 5 6 2-Octanol 5 10 1-Octanol 2-Octene 24 (2-Octanol 45 90 (2-Phenyl-69 5 48 Styrene ethanol 22 31 1-Phenyllethanol d-Methyl-2-Phenyl-71 5 1-propanol styrene

Hydroboration-Oxidation Reaction of Alkenes<sup>a</sup>) Table 3.

a) All the reactions were conducted at 65  $\,^{\circ}\text{C}$  by the reagent system; alkene : NaBH4 : Cp2TiCl2 : 18-crown-6 = 5 : 5 : 1 : 1. b) GLC yields based on alkenes used.

and 3 promotes the catalytic hydroboration of alkenes to give sodium alkylborohydrides, presumably via the alkene coordinated Ti complex 2.



PhC=CR + NaBH4 
$$\frac{1}{\text{THF}, 18-\text{crown-6}} \xrightarrow{H^+} \xrightarrow{Ph}_{H^-}C=C_{H}^{-R} + \xrightarrow{Ph}_{H^-}C=C_{R}^{-H}$$
  
R = H, Et, or Ph

The hydroboration of alkynes with  $NaBH_4$  in THF was also catalyzed by the complex 1. Initial products of this reaction were sodium alkenylborohydrides which upon protonolysis gave the corresponding alkenes. The results are shown in Table 4.

It has been shown that in the hydroboration of terminal alkynes with diborane, the formation of dihydroborated products usually predominates.<sup>4,5)</sup> In contrast to this, the titanium complex catalyzed hydroboration with NaBH4 affords preferentially monohydroborated products even in the presence of excess NaBH4. In the hydroboration of internal alkynes, the formation of *cis*-alkenes predominates in the initial stage. However, the detailed studies strongly suggested that in the presence of excess NaBH4, the isomerization of the *cis*-isomers to the *trans*-isomers occurs during the reaction.<sup>6</sup>

Table	4.	Hydroboration of Alkynes with NaBH4 in the Presence of Tita	nium
		Complex in THF <sup>a)</sup>	

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Alkyne	Reaction time / h	Product(s)	Yield(s) of product(s) / % <sup>b)</sup>	Recovered alkyne / %
C6 <sup>H</sup> 11 <sup>C≡CH</sup>	8	С6H11CH=CH2	74	5 <sup>c</sup> )
PhC≡CH	3	PhCH=CH <sub>2</sub>	70	20 <sup>a</sup> )
PhC≡CEt	14	cis-PhCH=CHEt	41	trace
		<i>trans-</i> PhCH=CHEt	51	
PhC≡CPh	23	cis-PhCH=CHPh	68	trace
		<i>trans-</i> PhCH=CHPh	26	

a) All the reactions were conducted at 65 °C by using the reagent system;
alkyne : NaBH4 : Cp<sub>2</sub>TiCl<sub>2</sub> : 18-crown-6 = 5 : 5 : 1 : 1. b) Yields based
on alkynes used. c) Octane was obtained as a by-product in a 9% yield.
d) Ethylbenzene was obtained as a by-product in a 3% yield.

## References

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- 6) In the case of 1-phenyl-1-butyne, the reaction mixture obtained by the hydroboration was quenched by CH<sub>3</sub>COOH at appropriate intervals. The product analyses showed that the mixture contains the *cis*-and *trans*-isomers in a 83:17 ratio after 6 h, in a 45:55 ratio after 14 h and in a 30:70 ratio after 20 h.

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